

# The Kinetics of F-Center Aggregation Under Irradiation: Many-Particle Effects in Ionic Solids

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## Abstract

The accumulation kinetics of primary Frenkel defects created in solids under permanent irradiation is calculated using the microscopic formalism of many-particle densities. It is based on the Kirkwood superposition approximation for three-particle densities as described in our previous paper [V. N. Kuzovkov and E. A. Kotomin, *Physica Scripta* 47, 585 (1993)]. This formalism is generalized in this paper by incorporating the elastic attraction between similar defects (called in ionic solids F-centers) which causes their efficient aggregation. It is shown that the aggregation process starts only if the dose rate and elastic attraction energy exceed certain critical values; it also happens in the limited temperature interval, in agreement with experimental data known for NaCl crystals. Results obtained are compared with those of the mesoscopic approach.

## 1. Introduction

The irradiation of solids of any nature (metals, semiconductors, insulators) with high-energy particles or electrons produces Frenkel defects-pairs of interstitial atoms and vacancies [1–7]. In alkali halides,  $MeX$ , primary Frenkel defects – F and H centers – are neutral defects with respect to the crystalline lattice; they are anion vacancy with trapped electron and  $X_2^-$  quasimolecule formed by  $X^0$  atom with a regular  $X^-$  anion, respectively. Both in metals and ionic solids vacancies are slowly mobile, whereas interstitials start to migrate at much lower temperature, typically about 30 K in alkali halides [3]. Therefore, even at moderate temperatures, the process of radiation-induced defect accumulation is diffusion-controlled. Numerous studies – both theoretical and experimental – were devoted in particular to the kinetics of F-center accumulation in alkali halides under irradiation [8–21]. Of special interest in recent years was the kinetics of defect aggregation in the form of colloids; in alkali halides irradiated at high temperatures and high doses bubbles filled with  $X_2$  gas and metal particles of several nm in size were observed [21].

Several theoretical formalisms were developed for describing this phenomenon, which could be classified into three general categories: (i) macroscopic theory [22–24], which is based on the rate equations for macroscopic defect concentrations; (ii) mesoscopic theory [25–27] operating with space-dependent local concentrations of point defects, and lastly (iii) microscopic theory [28–30] based on the hierarchy of equations for many-particle densities (in principle, it is infinite and contains complete information about all kinds of spatial correlation within different clusters of defects).

More information about these approaches and their advantages readers could find in Refs [26–28, 30]; in this paper we will focus on the further improvement of the

microscopic approach to the defect aggregation developed by us in Ref. [31], via taking into account elastic attraction between point defects. It will be shown that particle interaction plays a decisive role in the aggregation process. Section 2 gives a brief summary of the modification of kinetic equations used in calculations, Section 3 presents results for a particular case of F-center aggregates well studied in NaCl crystals, whereas in Section 4 general predictions of our approach are compared with recent findings of the mesoscopic approach [27].

## 2. The basic kinetic equations

The basic ideas of the microscopic formalism operating with the so-called many-point (MP) particle densities we use hereafter have been described in detail in Ref. [28] and applied to the accumulation kinetics of non-interacting particles in Ref. [31]. Note only that these densities,  $\rho_{mm}(r_1, r_2, \dots, r_m; r'_1, r'_2, \dots, r'_m; t)$  form an infinite hierarchy of coupled kinetic equations; therefore their practical use needs some decoupling procedure, e.g. by means of the Kirkwood superposition approximation. Using the latter, we arrive at several closed kinetic equations, containing macroscopic concentrations (simple or one-particle densities),

$$\rho_{1,0}(r, t) = n_A(t), \quad \rho_{0,1}(r', t) = n_B(t) \quad (1)$$

and three joint correlation functions describing similar particle spatial correlations,  $X_A(r, t)$ ,  $X_B(r, t)$  (pairs  $A-A$ ,  $B-B$ , respectively), and those of dissimilar particles,  $Y(r, t)$  (pairs  $A-B = B-A$ ):

$$\begin{aligned} \rho_{2,0}(r_1, r_2; t) &= n_A^2(t) X_A(|r_1 - r_2|, t), \\ \rho_{0,2}(r'_1, r'_2; t) &= n_B^2(t) X_B(|r'_1 - r'_2|, t), \\ \rho_{1,1}(r_1; r'_1; t) &= n_A(t) n_B(t) Y(|r_1 - r'_1|, t). \end{aligned} \quad (2)$$

We consider in this study the case of instant annihilation of dissimilar particles, leading to the standard Smoluchowski boundary condition for the joint densities,  $Y(r \leq r_0; t) \equiv 0$  and permitting us to simplify maximally the kinetic equations under study. The correctness of the Kirkwood superposition approximation for these problems was shown more than once [28, 30, 32].

The general basic equations describing particle accumulation kinetics in a wide range of temperatures were derived in Ref. [31]; they cover situations from entirely immobile to highly mobile particles, but ignoring their elastic interactions. In this paper, we consider effects of diffusion-controlled particle aggregation, which occurs when the particles' mobility is high enough. This allows us to neglect

the contribution of a recombination of particles  $A$  due to their birth directly within the annihilation sphere around pre-existing dissimilar particles  $B$  (and vice versa) compared to the result of diffusive dissimilar-particle drift to each other. Using the dimensionless units  $\xi = pv_0 r_0^2/D$ ,  $r' = r/r_0$ ,  $D_v = 2D_v/D$ ,  $t' = Dt/r_0^2$ , and  $n'(t) = n(t)v_0$  ( $v_0 = 4/3\pi r_0^3$  is the volume of recombination sphere) we arrive at the simple equations for the uncorrelated particle creation when at their birth no geminate (correlated)  $AB$  pairs are formed:

$$\left. \frac{dn(t)}{dt} \right|_{cr} = \xi, \quad (6)$$

$$\left. \frac{\partial Y(r, t)}{\partial t} \right|_{cr} = \frac{2\xi}{n(t)} \{1 - Y(r, t)\}, \quad (7)$$

$$\left. \frac{\partial X_v(r, t)}{\partial t} \right|_{cr} = \frac{2\xi}{n(t)} \{1 - X_v(r, t)\}, \quad v = A, B. \quad (8)$$

The relevant contributions to the kinetic eqs (6)–(8) from particle diffusion and recombination are (cf. [28])

$$\left. \frac{dn(t)}{dt} \right|_{diff+rec} = -3K(t)n^2(t); \quad K(t) = \left. \frac{\partial Y(r, t)}{\partial t} \right|_{r=1}; \quad (9)$$

$$\left. \frac{\partial Y(r, t)}{\partial t} \right|_{diff+rec} = \nabla[\nabla Y(r, t) + Y(r, t)\nabla\phi(r, t)] - 3K(t)n(t)Y(r, t) \sum_{v=A, B} J[X_v], \quad (10)$$

$$\left. \frac{\partial X_v(r, t)}{\partial t} \right|_{diff+rec} = D_v \nabla[\nabla X_v(r, t) + X_v(r, t)\nabla\phi_v(r, t)] - 6K(t)n(t)X_v(r, t)J[Y]. \quad (11)$$

Here,  $K(t)$  is the reaction rate and the functional  $J[Z]$  for  $d = 3$  under study is defined as

$$J[Z] = \frac{1}{2r} \int_{|r-1|}^{r+1} [Z(r' - 1) - 1]r' dr', \quad Z = X, Y. \quad (12)$$

The quantities  $\phi(r, t)$  and  $\phi_v(r, t)$  in eqs (9)–(11) are the mean-force potentials; their self-consistent derivation in the Kirkwood approximation was presented in Ref. [33]. In the dimensionless units these potentials read

$$\begin{aligned} \nabla\phi(r, t) = & \left\{ \nabla U_{AB}(r) + \frac{3D_A}{4\pi D} \left[ \int \nabla U_{AA}(r^*) X_A(r^*, t) Y(r', t) dr' \right. \right. \\ & + n(t) \left. \int U_{AB}(r^*) Y(r^*, t) X_B(r', t) \right] \\ & + \frac{3D_B}{4\pi D} \left[ n_B(t) \int \nabla U_{BB}(r^*) X_B(r^*, t) Y(r', t) dr' \right. \\ & \left. \left. + n(t) \int \nabla U_{AB}(r^*) Y(r^*, t) X_A(r', t) dr' \right] \right\}, \quad (13) \end{aligned}$$

$r^* = r - r'$ ; the equation for  $\phi_A(r, t)$  is similar to eq. (13).

As is well known [34], neutral point defects in all solids interact with each other by the so-called elastic forces caused by overlap of deformation fields surrounding both defects. These forces are effectively attractive for both similar and dissimilar defects (interstitial–interstitial, vacancy–vacancy and interstitial–vacancy, respectively) and decay with the distance  $r$  between defects as

$$U_{AA}(r) = -\frac{\lambda_A}{r^3}, \quad U_{AB}(r) = -\frac{\lambda}{r^3}. \quad (14)$$

We have to cut off elastic interactions at the short relative distances of the order of  $r_0$  due to the discreteness of the crystalline lattice [35]:  $U_{AA}(r \leq r_0) = U_{AA}(r_0)$ ;  $U_{AB}(r \leq r_0) = U_{AB}(r_0)$ . Finally, introducing two distinctive parameters

$$r_A = (\lambda_A/kT)^{1/3}, \quad r_E = (\lambda/kT)^{1/3}, \quad (15)$$

the dimensionless interaction potentials,  $U'(r) = U(r)/kT$ , finally read

$$\begin{aligned} U_{AA}(r) = & \begin{cases} -(r_A/r_0)^3, & r \leq 1, \\ -(r_A/r_0)^3/r^3, & r > 1, \end{cases} \\ U_{AB}(r) = & \begin{cases} -(r_E/r_0)^3, & r \leq 1, \\ -(r_E/r_0)^3/r^3, & r > 1. \end{cases} \end{aligned} \quad (16)$$

The accumulation kinetics under study is defined by three dimensionless parameters:  $\xi$ ,  $r_A/r_0$  and  $r_E/r_0$ ; all three depend on the temperature. The physical meaning of the former parameter is quite obvious: The value of  $\tau_D = r_0^2/D$  is a distinctive time required for particle passage the distance  $r_0$ , i.e. to leave the recombination sphere. Another distinctive time  $\tau_p = 1/pv_0$  is the mean time between two particle births in a given volume,  $v_0$ . Therefore, their ratio,  $\xi = \tau_D/\tau_p$ , characterizes which of the two effects – particle production or diffusion – is predominant at a given temperature (particle diffusivity).

The joint correlation functions  $X_A$ ,  $X_B$  characterize an aggregation effect of similar particles; their random distribution is taken as the initial condition,  $X_{A, B}(r, 0) \equiv 1$ . By definition, these joint correlation functions give a ratio of the probability density to find a pair of defects  $vv'$  ( $vv' = A, B$ ) at a given relative distance  $r$  to that for a random distribution,  $r \rightarrow \infty$ , that is these functions are normalized asymptotically as  $X_v(r \rightarrow \infty, t) \equiv 1$ . In the limiting case of small particle concentrations one can neglect the non-linear terms in eq. (11) which gives us the simplest estimate of the correlation function for similar particles. At relatively long times it reaches the steady-state and gives just the Boltzmann distribution

$$X_A^0(r, \infty) \approx \exp \{-U_{AA}(r)\}. \quad (17)$$

The increase in time deviation of functions  $X_A(r, t)$  above the asymptotic value, observed more than once in our previous calculations [28–30] means formation of the non-Poissonian particle distribution via enriched concentration of pairs of similar particles,  $A-A$ , or  $B-B$ , at their short relative distances, which is nothing but their aggregation.

To characterize aggregation of similar particles, it is convenient to use not only their correlation functions, but an integral quantity, characterizing the number of particles in aggregates. Indeed, the value of  $C_A(r, t) = n_A(t)X_A(r, t)$  has the physical sense of the average concentration of particles  $A$  at the distance  $r$  from another particle  $A$  in the origin of coordinates. Therefore, the quantity  $\delta C_A(r, t) = n(t)[X_A(r, t) - 1]$  gives us the surplus in the concentration with respect to the Poisson (random) particle distribution. This is why the integral quantity

$$\langle N \rangle = \int_0^{r^*} \delta C_A(r, t) dr \quad (18)$$

gives us the average number of particles  $A$  in an aggregate surrounding arbitrary chosen central particle  $A$ . Calculu-

lations demonstrate a sharp maximum of  $X_A(r, t)$  around  $r \approx r_0 = 1$  which makes a major contribution into  $\langle N \rangle$ . Typically, at larger distances  $X_A$  drops a little bit below its asymptotic value of unity and then slowly approaches it from below; therefore the distinctive distance  $r^*$  where  $X_A(r^*, t) = 1$  could be defined as the aggregate boundary. The quantity of  $\langle N \rangle$  is convenient to complement by another distinctive characteristics which is called the aggregate size,

$$\langle R \rangle = \frac{1}{\langle N \rangle} \int r \delta C_A(r, t) dr. \quad (19)$$

If no aggregation occurs, the joint correlation function coincides with eq. (17) and the value of the integral  $\langle R \rangle$ , eq. (19), is divergent, since as  $r \rightarrow \infty$ ,  $\delta C(r, t) \propto r^{-3}$  whereas  $dr \propto r^2$  only. (Due to a limited integration interval we obtain in numerical calculations not infinity but big numbers, of the order of  $10^2$ .) However, as soon as the aggregation process becomes important, the correlation function  $X_A(r, t)$  drops much faster than eq. (17), the integration interval shortens down to the values close to the recombination radius  $r_0$  and thus the quantity  $\langle R \rangle$  turns out to be a much smaller value, of the order of unity (in units of  $r_0$ ). Therefore, only the parallel study of the time-development of both quantities –  $\langle N \rangle(t)$  and  $\langle R \rangle(t)$  – gives us a complete picture of the aggregation process.

Analytical calculations of the aggregation process kinetics in terms of this approach are presented in Ref. [36]. It is shown there that the aggregation occurs only if the distinctive dimensionless parameter  $\psi$  is positive:

$$\psi = \frac{\lambda_A}{kTr_0^3} + \frac{1}{4} \ln(pv_0r_0^2/D) \geq 0. \quad (20)$$

It gives the marginal dose rate  $p_c$  as a function of the elastic interaction between similar defects and the temperature:

$$p_c = \frac{3D_0}{4\pi r_0^5} \exp[-E_A/kT - 4\lambda_A/kTr_0^3],$$

$$D_A = D_0 \exp(-E_A/kT); \quad (24)$$

where  $A = v, I$  (vacancy or interstitial).

The marginal dose rate  $p_c$  necessary for aggregation is the smaller, the lower the temperature is, stronger elastic attraction of similar particles and slower their diffusion (i.e. greater the activation energy for hopping). This conclusion is in a complete qualitative agreement with the results obtained recently in terms of a quite different mesoscopic approach to be discussed in Section 4.

To get the reference point for many-particle effects in defect accumulation, the saturation concentration,  $n(t \rightarrow \infty)$ , could be easily estimated in the linear approximation [29], i.e. neglecting in the kinetics equations (10) and (11) non-linear terms with the functionals  $J[Z]$  responsible for many-particle effects. In this manner one easily gets from eqs (6), (10) and (11) the dimensionless saturation concentration

$$n_0 = n(\infty) \approx \sqrt{\frac{p}{4\pi Dr_0}} \approx \sqrt{\frac{\xi r_0}{3r_E}}. \quad (25)$$

Note that this concentration is governed by a sum of diffusion coefficients,  $D_1 + D_v$ , that is practically by  $D_1$ . In the temperature range of high mobilities the value of  $r_E$  usually

exceeds  $r_0$  no more than by a factor 2–3 and  $\xi \ll 1$ , that is,  $n_0 \approx \frac{1}{3} \sqrt{\xi} \ll 1$ .

At moderate defect mobilities  $n_0$  has a correction factor of  $(1 + \sqrt{3n_0})$  in the denominator of eq. (25) [31]. Lastly, in the regime of intensive aggregation one can expect  $n_0$  to be considerably lower than given by eq. (25) due to disappearance of single defects in their aggregates.

Our general theory will be illustrated in Section 3 for the set of parameters distinctive for NaCl crystals for which a lot of aggregation studies were done (see [22–24] for more detail). However, if one uses, as a test, eq. (25) in order to estimate the just-mentioned reference point – the saturation concentration without considerable aggregation – one immediately finds for the standard set of parameters – the activation energy of interstitial hops  $E_1 = 0.1$  eV [2, 3, 37], and  $D_0 = 10^{-3}$  cm<sup>2</sup>s<sup>-1</sup>,  $r_0 \approx 3$  Å,  $p = 7 \times 10^{12}$  cm<sup>-3</sup>s<sup>-1</sup> that at  $T = 15$  °C and 85 °C the calculated concentrations are  $n_0^{\text{th}} = 10^{12}$  cm<sup>-3</sup> and  $6.8 \times 10^{11}$  cm<sup>-3</sup>, whereas experimental values are much higher [8]:  $6 \times 10^{16}$  cm<sup>-3</sup> and  $10^{16}$  cm<sup>-3</sup>, respectively! Surprisingly, this puzzle has never been discussed in the extensive theoretical literature devoted to F-center aggregation [8–24]! Recently [27], an explanation of this fact has been suggested assuming that the effective diffusion coefficient for mobile interstitials is reduced considerably due to their periodical trapping by radiation-induced ( $v_s, v_c$ ) di-vacancies observed experimentally in Ref. [38]. Therefore, in this paper we adopted the effective activation energy in NaCl of  $E_1 = 0.37$  eV and  $D_0 = 2.6 \times 10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>, which approximate very well the experimental data obtained in the non-aggregation regime. For vacancies we use  $E_v = 0.9$  eV. Since the kinetics of interstitial accumulation was considered in Ref [36], here we concentrate on the F-center aggregation for which much more experimental information is available. It is known from the calculations for alkali halide crystals [39] that typical values of the elastic interactions between two interstitials and interstitial–vacancy are:  $\lambda_1 \approx 15$  eV Å<sup>3</sup> and  $\lambda \approx 5$  eV Å<sup>3</sup>, respectively. The elastic interaction energy between two vacancies is not exactly known and we accept for our semi-qualitative calculation done below the very moderate value of  $\lambda_v \approx 5$  eV Å<sup>3</sup>.

### 3. Results

Figure 1 shows the joint correlation function for vacancies for a fixed dose rate of  $p = 10^{17}$  cm<sup>-3</sup>s<sup>-1</sup> but varying the temperature from 0 °C to 150 °C. The two low-temperature curves – at 0 °C and 50 °C – decay monotonously with  $r$ , as it is predicted by eq. (17). However, as temperature increases further, curves 3 and 4 reveal a new type of behavior – they fall below the asymptotic value of  $X = 1$  and then approach it from below, as  $r \rightarrow \infty$ . Physically it means that an aggregate of similar defects arose which absorb similar defects nearby it due to which its concentration is reduced below the statistical level. The distinctive aggregate's size  $R^*$ , defined as  $X(R^*) = 1$ , is about 1.5–2 $r_0$  for  $T = 100$  °C and 150 °C. Note also that the correlation curve 4 goes below curve 3 at short distances which means that at such high temperatures aggregation of very mobile vacancies is less efficient. In other words, there exists an optimal temperature for defect aggregation (see below). Figure 2 characterizes the effective attraction between F-centers with and without

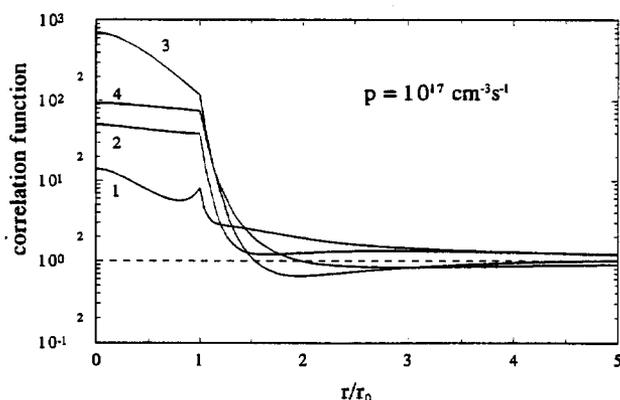


Fig. 1. The joint correlation functions  $X_v(r)$  at  $t = 10^{10}$  s for similar defects (V-V) for the temperatures 0°C (curve 1), 50°C (curve 2), 100°C (curve 3) and 150°C (curve 4). Note that only in the cases 3 and 4 the aggregation really takes place: the correlation function crosses the asymptotic values of  $X = 1$  (see text). The elastic interaction energy  $\lambda_v = 5 \text{ eV } \text{Å}^3$ .

aggregates. In the aggregation regime an additional short-range force arises (curve 2) which has a many-particle nature and arises to the non-linear terms in eq. (13) at  $r < 1$ .

Our microscopic formalism cannot give the distribution function over aggregate sizes, but having calculated a mean number of defects in an aggregate, eq. (18), we can assume validity of the Poisson distribution (for the moderate aggregation efficiency)

$$\Phi(m) = \exp(-\langle N \rangle) \frac{\langle N \rangle^m}{m!}, \quad (26)$$

and thus calculate the concentration of dimers ( $F_2$ ) centers,  $n(F_2) = n(F)\Phi(1)$ , trimers,  $n(F_3) = n(F)\Phi(2)$  etc. From this point of view, it is reasonable to define as aggregates only those defect clusters where a portion of dimers is not very small compared to the concentration of single F-centers. Say, if  $n(F) = 10^{18} \text{ cm}^{-3}$ ,  $n(F_2)$  should be  $\geq 10^{15} \text{ cm}^{-3}$ , i.e.  $\langle N \rangle \geq 10^{-3}$ . Such a definition corresponds to a very weak, marginal aggregation process which is our primary interest here.

The F-center saturation concentration as a function of temperature and dose rate are plotted in Fig. 3. In line with general theory, eq. (25), it is higher for large dose rates and low temperatures. What is non-trivial here is the aggregation region which lies between the two dashed lines. The left line corresponds to the above-given aggregate definition,  $X(R^*) = 1$ . The right dashed line corresponds to the second

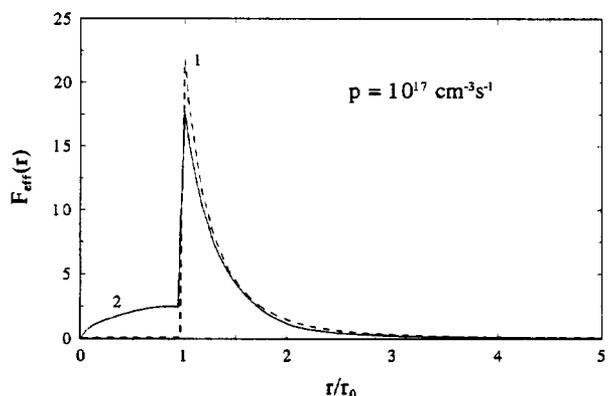


Fig. 2. The effective attraction force between vacancies. Curve 1:  $T = 0^\circ\text{C}$ , no aggregation; curve 2:  $T = 100^\circ\text{C}$ , aggregation occurs (note an additional attraction at short distances).

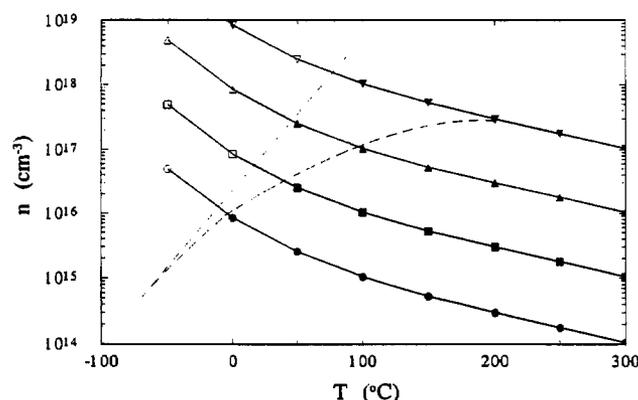


Fig. 3. The saturation concentrations as a function of the temperature for different dose rates:  $p = 10^{11} \text{ cm}^{-3} \text{ s}^{-1}$  (●),  $10^{13} \text{ cm}^{-3} \text{ s}^{-1}$  (■),  $10^{15} \text{ cm}^{-3} \text{ s}^{-1}$  (▲) and  $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$  (▼). The two dashed lines show the temperature interval in which the aggregation takes place (see text).

aggregation condition discussed above – the concentration of dimer centers,  $F_2$ , should not be three orders of magnitude less than that for single F-centers. This conclusion, about the existence of an optimal temperature for the aggregation for a given dose rate, is in agreement with our analysis of the joint correlation functions (Fig. 1) and the experimental data on NaCl crystals [40].

A large body of experiments (e.g. [9, 12, 13]) deals with the kinetics of dimer center accumulation; it was observed experimentally that  $n(F_2)$  often increases as squared  $n(F)$  concentration. In our formalism,  $n(F_2) \approx \langle N \rangle n(F)$ . As is well seen in Fig. 4,  $\langle N \rangle$  turns out to be a linear function of  $n(F)$ ; in a wide range of defect concentrations and dose rates  $\langle N \rangle \approx 10^{-20} \text{ cm}^{-3} n(F)$ . The slope of this curve depends only slightly on the elastic attraction energy,  $\lambda_v$ , between F-centers. Deviation from the quadratic law begins only at quite high defect concentrations,  $n \geq 10^{18} \text{ cm}^{-3}$ . These findings confirm results of an earlier rate-equation model [9–12].

The time development of the F-center concentration, up to saturation, and the mean number of particles in aggregates, are shown in Fig. 5(a), (b). The  $n_0$  values are well described by eq. (25), valid for weakly aggregated systems;  $n_0 \propto \sqrt{p}$ . The concentrations are saturated at the time  $\tau_0 \propto \sqrt{p^{-1}}$ .

Figure 6 shows a similar dependence for a fixed dose rate but varying the temperature (F-center mobility). As expected from eq. (25), the higher temperature, the more intensive defect recombination and thus the lower the saturation con-

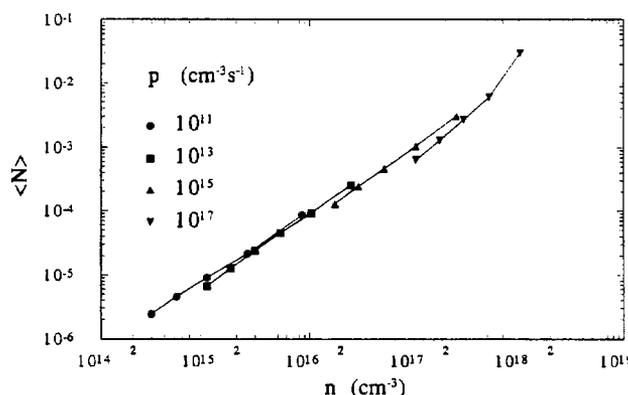


Fig. 4. The dependence of the mean number of particles in the aggregate, eq. (18), as a function of the F-center concentration.

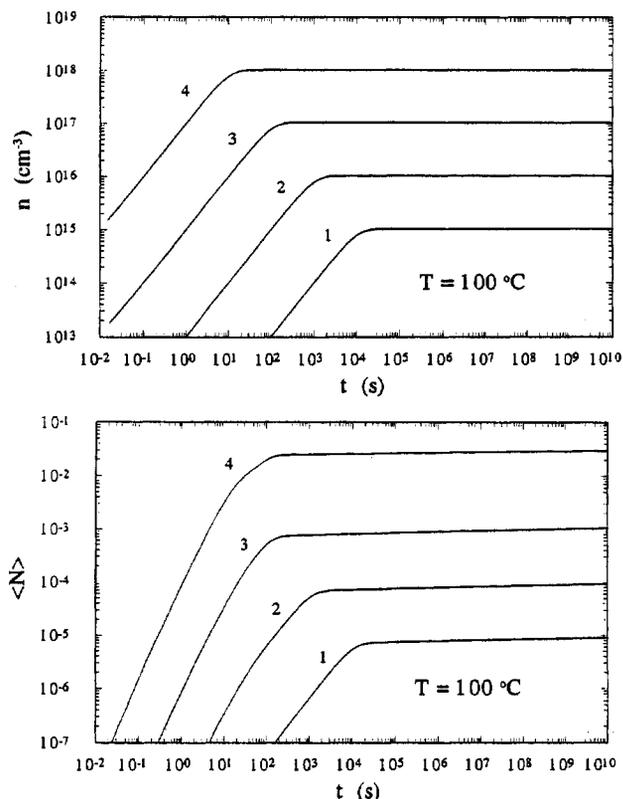


Fig. 5. (a) F-center concentration as a function of time for the dose rate:  $10^{11} \text{ cm}^{-3} \text{ s}^{-1}$  (curve 1),  $10^{13} \text{ cm}^{-3} \text{ s}^{-1}$  (curve 2),  $10^{15} \text{ cm}^{-3} \text{ s}^{-1}$  (curve 3) and  $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$  (curve 4); (b) The same for mean numbers of particles in aggregates; note that these curves do not saturate but continue to grow up slowly.

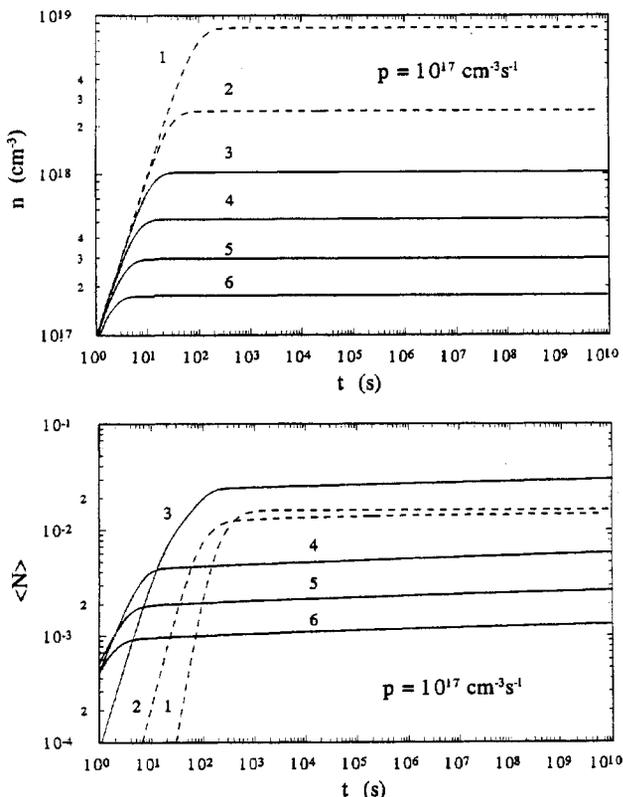


Fig. 6. (a) F-center concentration as a function of the temperature:  $0^\circ \text{C}$  (curve 1),  $50^\circ \text{C}$  (curve 2),  $100^\circ \text{C}$  (curve 3),  $150^\circ \text{C}$  (curve 4),  $200^\circ \text{C}$  (curve 5) and  $250^\circ \text{C}$  (curve 6). The dashed line indicates that no aggregation takes place at these temperatures (for a given dose rate of  $p = 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ ); (b) The same for the mean number of defects in aggregates. Dashed curves are obtained by integrating over sphere with the radius  $2r_0$ . Note the aggregation reaches its maximum at  $100^\circ \text{C}$  (curve 3). Full curves do not saturate with time-slow aggregation continues.

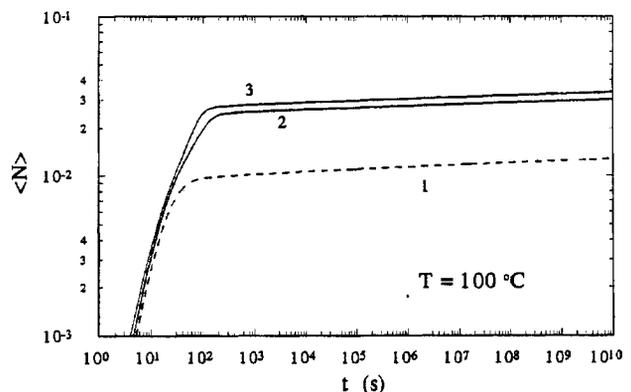


Fig. 7. A critical role of the elastic interaction energy between vacancies: no aggregation occurs for  $\lambda_v = 4 \text{ eV } \text{Å}^3$  (dashed curve 1) but it starts for the larger values of  $\lambda = 5 \text{ eV } \text{Å}^3$  (curve 2) and  $8 \text{ eV } \text{Å}^3$  (curve 3).

centration. Curve 3 in Fig. 6(b) confirms once more that  $T \approx 100^\circ \text{C}$  is optimal for a given dose rate of  $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$  – at higher temperatures a portion of  $F_2$  centers decreases.

Lastly, a decisive role of the elastic attraction between F-centers in their aggregation is seen in Fig. 7. For small attraction energy,  $\lambda_v$ , (curve 1) aggregation does not hold even at as great dose rates as  $p = 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ . However, as far as  $\lambda_v$  exceeds some (quite moderate) critical value about  $5 \text{ eV } \text{Å}^3$ , the number of dimer centers is increased by a factor of 2–3 (curves 2 and 3).

#### 4. Discussion

As it has been demonstrated in this paper, the microscopic approach predicts the existence of the marginal value of elastic attraction energy between similar defects – F-centers – which initiates the aggregation process – the further accumulation kinetics, when the aggregation started to occur, depends only slightly on the interaction energy,  $\lambda_v$ . Another important conclusion confirming results of macroscopic studies [22, 24] is that the aggregation occurs only in a limited temperature range – at low temperatures it disappears due to very slow mobility of F-center, whereas at high temperatures relatively weak elastic interaction can no longer keep highly mobile defects together in the aggregate. On the other hand, for a given temperature there exists a certain critical dose rate necessary for the aggregation process initialization, and it increases with the temperature increase [12, 20]. All these findings are in agreement with experimental data for NaCl crystals, discussed also in Section 3, and the recent mesoscopic studies [27]. In that paper the critical dose rate was found to be

$$\ln p_c \geq \ln D + 2 \ln \frac{kT}{\Delta_{e1}} + \ln \left[ \left( 1 + \frac{D_v}{D_1} \right)^2 4\pi r_0 \right] \quad (27)$$

where  $\Delta_{e1}$  is defined by the combination of the elastic interaction energies between similar and dissimilar defects:

$$\Delta_{e1} = \frac{4}{3} \pi \left[ \lambda_1 + \frac{D_v}{D_1} \lambda_v - \left( 1 + \frac{D_v}{D_1} \right) \lambda \right] \quad (28)$$

On the other hand, the present microscopic approach leads to the following critical dose rate, eq. (24):

$$\ln p_c \geq \ln D - \frac{4\lambda_A}{kTr_0^3} + \ln \frac{3}{4\pi r_0^5}. \quad (29)$$

Both eqs (28) and (29) have the same dependence on the relative diffusion coefficient,  $D = D_1 + D_v$ , but different dependence on the elastic interaction between defects. However, in both cases the stronger similar defect attraction, the lower is the critical dose rate. In the mesoscopic approach this effect is less pronounced (logarithmic vs. linear dependence) and here  $p_c$  is considerably higher, since this approach is able to detect only those mesoscopic-size aggregates which are already well-developed – unlike the microscopic formalism which is able to detect the marginal aggregation effects.

Lastly, the present theory confirms the quadratic dependence between the concentration of dimer  $F_2$ -centers (also called M-centers) and concentration of single F-centers – observed more than once experimentally [9, 12, 13].

#### Note added in proof

In Ref. [22] the simple eq. (16) was suggested for the saturation concentrations. Despite the fact that it describes the experimental saturation concentrations better than our eq. (25), the range of its applicability is not clear; in particular, it predicts unlimited growth of concentrations if F centers are immobile.

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